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THESIS

THE SOLUBILITY OF CUPRIC HYDROXIDE AND CUPRIC OXIDE IN WATER AT VARIOUS TEMPERATURES

A Study of the Phase Relations between Cupric Hydroxide and Water

by

Maurice M. Pechet, B. Sc.

Edmonton, Alberta April, 1940.

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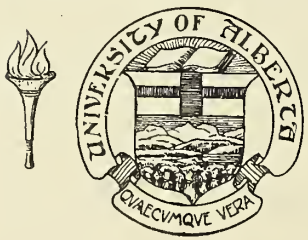

THESIS

THE SOLUBILITY OF CUPRIC HYDROXIDE AND CUPRIC OXIDE IN WATER AT VARIOUS TEMPERATURES

A Study of the Phase Relations
between Cupric Hydroxide and Water.

Submitted in Partial Fulfilment of the
Requirements for the Degree of Master of Science.

By

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Carried out under the direction of Dr. J. W. Shipley.

Time devoted to thesis work was 7.0 months.

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THE SOLUBILITY OF CUPRIC HYDROXIDE AND CUPRIC OXIDE IN WATER AT VARIOUS TEMPERATURES.

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INTRODUCTION

The purpose of this investigation was to determine the solubility of cupric hydroxide and cupric oxide in water, over the temperature range from ordinary temperatures to the boiling point. A careful search in the chemical literature revealed very few data on the subject.

Remy and Kuhlman[1] assuming that the oxide goes into solution in water as cupric hydroxide report its solubility to be 5.4 mgms. per litre (expressed as cupric oxide.) or 6.7×10^{-5} moles per litre at 20°C (expressed as cupric hydroxide.) They used a conductivity method and assumed complete dissociation of the hydroxide in solution. This result may be in error, as pointed out by Mohanlal and Dhar[2]. They found

that the hydroxide of copper in alkaline solution is colloidal, and the decrease in electrical conductivity is due to the adsorption of alkali by the hydroxide for its peptization and replacement of hydroxyl ions by cuprate ions.

Jellinek and Gordon[3], from e.m.f. measurements in concentration cells secured potentials from which the solubility of cupric hydroxide at a temperature of 15°C to 20°C gives a value of 3.49×10^{-5} moles per litre. But this result is not corrected for the changing activity coefficients of the ions.

Rakuzo Tomii, Eishin O'Kabbe and Shinichi Takeda[4], using a capillary electrode in the potentiometric determination of copper and from calculations of the inflection potential of the reaction

$$Cu^{++} + 2OH^{-} \longrightarrow Cu(OH)_2$$

found a value of 4.53×10^{-3} moles per litre for the solubility of cupric hydroxide. The temperature at which this value was obtained was not reported.

McDowell and Johnston[5] attempted to determine the solubility of cupric oxide in pure water. They were faced with the difficulty of the solution coming out colloidal unless the alkalinity exceeded 0.03N. They obtained a rough value for the solubility of cupric oxide in pure water using an electrometric titration with potassium ferrocyanide as precipitant. They obtained a value of 2.9×10^{-5} moles per litre at 25°C for the solubility of CuO in water or 3.57×10^{-5} moles per litre for $Cu(OH)_2$.

The determinations mentioned above, which depend on the measurement of electrical conductivity, are subject to error because of the susceptibility to extremely small traces of impurities. There is also a wide deviation in the results reported by different investigators. Consequently the present investigation was undertaken using a different method to confirm or otherwise, the values reported above and to add to the data by obtaining values at various temperatures.

The Preparation and Properties of Cupric Hydroxide

The gelatinous precipitates which are produced by mixing an alkaline solution with solutions of the salts of iron, chromium, copper, and many other metals show a high but variable molecular ratio of water to basic oxide. It is presumed that the water is held by adsorption or loose chemical combination, and is gradually lost as the product is dried. The composition of the dried product is thus largely fortuitous and in general definite hydrates of the metallic oxides are not formed under such uncontrolled conditions. A composition corresponding to a definite hydrate is therefore accidental, depending as it does on the method of formation, the method of drying, the temperature and the age of the sample. Precipitated oxides like ferric oxide which contain varying amounts of water adsorbed by the oxide particles are called hydrous

oxides to distinguish them from hydrates in which the water is chemically combined in definite stoichiometric proportions. The so called hydroxides of these metals are, therefore, more correctly described by the term hydrous oxides. On standing, the primary colloidal particles of the hydrous oxides grow and lose water spontaneously, causing the mass to assume a less gelatinous and a more granular character. This spontaneous transformation from a loose voluminous precipitate to a granular mass is accompanied by a decrease in the solubility, in the adsorbability, and in the peptizability of the compounds.

When a solution of NaOH is added in slight excess to a solution of a cupric salt, the gelatinous blue precipitate formed will under ordinary circumstances, quickly turn black. This change in color of the precipitate was first noticed while the latter was being filtered and washed. The change to the black color was apparently completed on exposure to air in less than

a week. However, following the method of Neville and Oswald[6], the precipitation was brought about in dilute solution at 0°C. The precipitate was carefully washed and air-dried without any change in color, but after remaining in contact with the atmosphere it began to darken.

The freshly made gelatinous precipitate is highly hydrous, containing according to van Bemmelen[7], more than 20 moles of water to 1 mole of cupric oxide even after pressing between porous earthenware. Exposure of this material to an artificially dried atmosphere at room temperature causes it to lose water continuously until its composition corresponds to the monohydrate $CuO.H_2O$ or $Cu(OH)_2$.

Various substances accelerate and other substances retard the change in color of the gelatinous blue precipitate. The change from blue to black is notably accelerated by small quantities of hydrogen peroxide in alkaline solution. According to Quartaroli[8], this action is still perceptible with 1 part of hydrogen peroxide

in 200 million parts of water, but when added after precipitation is complete hydrogen peroxide has no accelerating effect. The acceleration is very sensitive to temperature change decreasing with low temperatures. Ordinary distilled water contains traces of hydrogen peroxide, formed in the process of distillation, but below the sensitivity of the common reagents for hydrogen peroxide detection, such traces are according to Quartaroli, sufficient to act upon cupric hydroxide and accelerate the change from blue to black.

Chatterji and Dhar[9] state, that blue cupric hydroxide containing a trace of undecomposed copper salt is stabilized by the latter and does not turn black even at the boiling temperature. Pickering[10] believes that a number of basic cupric salts exist. Accordingly when cold dilute sodium hydroxide is added to a solution of copper sulphate, the basic salt $CuSO_4.3Cu(OH)_2$ is first precipitated which is only slowly converted by dilute alkali to $CuSO_4.9Cu(OH)_2$ and finally to the normal hydroxide.

Mehratra and Dhar[11] found that all the copper is precipitated from a solution of cupric sulphate by less than the equivalent quantity of sodium hydroxide, and that either the cupric and sulphate ions are adsorbed in equivalent amounts or some basic salt of the composition:

$3\ Cu(OH)_2.CuSO_4$ or $4CuO.SO_3.4H_2O$

is formed. He also found that cupric hydroxide prepared from cupric chloride is a better adsorbent than the hydroxide obtained from cupric sulphate. It is apparent therefore, that a copper hydroxide free from basic salt or adsorbed copper salt will be formed only in the presence of a slight excess of alkali. The precipitate will then contain adsorbed alkali which for some unknown reason appears to accelerate the darkening. Hence to obtain a clear blue product, precepitation should be carried out at 0° and the mother liquor removed by washing with iced water as rapidly as possible. The supernatant liquid should be neutral to phenolphthalein or give no test for cupric ion.

Losana[12] believing the blue precipitate to be $CuO.H_2O$ described experiments to show that $CuO.H_2O$ undergoes dehydration in two distinct ways. If dehydration takes place in the presence of a liquid, definite compounds corresponding to 3-, 4-, and $8CuO.H_2O$ are formed as shown by the heating curves obtained at various temperatures. The dry compound loses water giving 3-, 4-, 6-, and $8CuO.H_2O$ but not $7CuO.H_2O$. The compound $8CuO.H_2O$ also loses small amounts of water but only at red heat. Losana believes that the various hydrates may be considered to be definite and quite stable compounds. Champetier and Thuau[13] using X-rays showed that the dehydration of cupric hydroxide at 105° to cupric oxide denies the existence of the intermediate oxide $4CuO.H_2O$. The brown oxide to which this formula has been attributed is therefore not a distinct chemical compound, but the anhydride CuO, retaining either some $Cu(OH)_2$ or some adsorbed water.

However Binder[14] states, that of all the nine compounds $mCuO.nH_2O$ (m=1 to 3, n=3 to 1)

reported only copper hydroxide exists. The existance of the other hydrates is due to complications caused by the presence of excess alkali in the precipitation, or of water adsorbed by colloidal copper hydroxide and removed to varying degrees.

In the case of the precipitate formed by the action of an alkali with cupric salts the evidence has been inconclusive and the opinion has been divided as to the existence of a definite compound corresponding to the composition $CuO.H_2O$ or $Cu(OH)_2$. The literature in regard to this question is extensive. Many authors refer to the blue precipitate as copper hydroxide while others consider it a finely divided form of hydrous copper oxide which darkens upon dehydration and agglomeration.

In the absence of conclusive evidence to the contrary, it was believed by Weiser[15] that the blue gel was hydrous cupric oxide rather than cupric hydroxide and that the variation in color from blue to black was due to difference in particle size. It is now known that such is not the

case, for the blue and the black precipitates give entirely different X-ray diffraction patterns. Thus Neville and Oswald[6] obtained the X-ray diffraction pattern for the blue precipitate thrown down:

(1) at 0°C. from cupric nitrate with sodium hydroxide and dried at room temperature.

(2) at room temperature from cupric nitrate and sodium hydroxide in presence of gelatin to stabilize it and dried at 55°C.

(3) the same as (2) but not dried.

This blue precipitate had a crystal structure distinctly different from the black substance obtained:

(1) from the moist black gel which forms spontaneously from the blue gel.

(2) from the black product formed by heating the dry blue powder to 105°C.

(3) the same as (2) dried over a Bunsen burner.

Thus the blue substance is not simply hydrous cupric oxide in finely divided form but is a definite compound, either $Cu(OH)_2$ or $CuO.H_2O$. These

observations confirm the work of Posnjak[16], who showed further that the blue gelatinous precipitate usually obtained is crystalline, and is identical with the microscopically crystalline preparations which are known to have the composition $CuO.H_2O$.

From their work Neville and Oswald[6] believe that three factors may be involved in the transformation of the blue gelatinous precipitate to the black oxide. These factors are:

1. Change in chemical constitution involving the release of a molecule of water.

2. Change in crystal structure.

3. Increase in size of the primary particles.

With regard to the first factor, the loss of water does not appear to be a matter of simple dissociation of a hydrate and it is therefore concluded that the molecule has the constitution $Cu(OH)_2$ rather than $CuO.H_2O$. Bancroft[17] points out that if a definite hydrate of the composition $CuO.H_2O$ exists with a practically zero vapour pressure it should form from cupric oxide in the presence of water, but actually the reverse process takes place.

It was impossible to reverse the change from black cupric oxide to blue cupric hydroxide by boiling the black product in pure water. It has been noticed that the change in color of the precipitate from the blue to the black in contact with the mother liquid, or under water, after thorough washing or when being filtered, begins at certain nuclei and spreads in all directions. This effect is an illustration of a reaction occurring at the interface between two solid phases, in this case the phases are copper oxide and copper hydroxide. This is a general phenomenon and has been observed, for example, by Jones and Taylor[18] in the reduction of copper oxide to copper by means of carbon monoxide.

Kohlschutler and Tuscher[19] likewise believe, that the blue substance is copper hydroxide and that its change to the black oxide is not simply a molecular splitting off of water, but involves the internal neutralization of the ions resulting from the amphoteric dissociation of copper hydroxide. The mechanism is illustrated as follows:

$$Cu^{++} + 2OH^- \leftrightarrows Cu(OH)_2 \leftrightarrows CuO_2^{=} + 2H^+$$

$$2H^+ + 2OH^- \rightarrow 2H_2O$$

$$Cu^{++} + CuO_2^{=} \rightarrow 2CuO.$$

It is assumed that this process takes place between molecular complexes large enough to be of colloidal dimensions and that a definite degree of dispersion is necessary for the change. Too low or too high a dispersion represses the reaction. The same primary particles may give a loose aggregate which is favorable to dehydration or a dense aggregate which is more stable. Thus stabilization by an adsorbed basic salt or gelatin or by low temperature may be looked upon as a process of inhibiting the agglomeration of primary particles as they are transformed into a more compact mass by drying. This would be equally true whether one assumes the dehydration is the result of molecular dehydration or of 'internal neutralization' as a result of amphoteric dissociation.

Further evidence that the blue cupric hydroxide is distinctly different from cupric oxide was obtained by Veil[20] who found that the blue compound has a molecular coefficient of magnetization which is about three times as great

as the black cupric oxide.

Thus the conclusion is that the blue compound is cupric hydroxide and not finely divided copper oxide. The colored products intermediate between the blue and the black are believed to be mixtures of $Cu(OH)_2$ and CuO in varying amounts.

EXPERIMENTAL

1. METHODS OF PREPARING CUPRIC HYDROXIDE

(a) Preparation from Copper Nitrate and Sodium Hydroxide at Low Temperature

A 1.0N. solution of cupric nitrate (Reagent Quality) and a 1.25N. solution of sodium hydroxide (Reagent Quality) were cooled to 0°C. Equal volumes of these two solutions were mixed at this temperature with thorough stirring. Freshly boiled redistilled water which had been cooled to 0°C. was used to wash the precipitate by decantation and then on a suction filter until the washings showed no alkalinity to phenolphthalein. A voluminous, gelatinous precipitate was obtained, which darkened upon air-drying, and after exposure to air for a week turned completely black.

(b) Preparation from Cupric Nitrate and Sodium Hydroxide in the Presence of Gelatin to Stabilize the Copper Hydroxide

If, in the preparation of copper hydroxide, sufficient alkali is added to avoid the presence of basic salts, either an inconveniently low temperature must be employed throughout or some stabilizing agent must be used at room temperature. Gelatin is well known for its stabilizing properties. The stabilizing action of gelatin may be looked upon as a process of inhibiting the agglomeration of the primary particles as they are transformed into a compact mass by drying. It is well known that gelatin exhibits such protective action both in preventing the agglomeration of fine particles and in interfering with crystal growth.

A 1.0N. solution of cupric nitrate and 1.25N. solution of sodium hydroxide were cooled to 0°C. Before precipitation 0.5 ml. of 5 percent gelatin solution were added so that the concentration of gelatin was 0.025 percent

by weight of the combined solutions. The precipitate was washed by decantation with freshly boiled redistilled water which had been cooled to room temperature, until the washings were neutral to phenolphthalein. Neville and Oswald[6] showed that the gelatin is completely removed from the solution by adsorption on the precipitate. This precipitate was dried over $CaCl_2$ for four months, and at the end of this period the precipitate had taken on a dark green color and appeared very granular.

(c) Preparation by the Hydrolysis of Blue - Violet Copper Ammonium Sulphate, at Low Temperature

Bonsdorff[21] used this method of hydrolysing the blue - violet copper ammonium sulphate to prepare cupric hydroxide. Compared with the difficulties mentioned above in the preparation of the cupric hydroxide by the action of alkali on a cupric salt, a product

easier to prepare and to wash was suggested by this method.

Copper sulphate pentahydrate was twice recrystallized from water and a 1.0N. solution of copper sulphate prepared. To 300c.c. of the copper sulphate solution, cooled to 0°C, 140c.c. of dilute ammonium hydroxide were added, slowly with constant stirring, until the precipitate first formed redissolved giving the characteristic clear deep blue solution of copper ammonia complex. 450c.c. of 1.25N. sodium hydroxide solution cooled to 0°C. were then added slowly with constant stirring. The cupric hydroxide precipitated out, and the completeness of precipitation was tested for by removing some of the clear supernatant liquid and adding a drop of sodium hydroxide. Freshly boiled, redistilled water which had been cooled to 0°C. was used to wash the blue precipitate by decantation and on a suction filter until the washings showed no alkalinity to phenolphthalein.

The precipitate so obtained was of the same blue color as that prepared from the alkali solution and a cupric salt, but it was not gelatinous in nature. Although it was granular in appearance, no definite crystals could be seen under the microscope, however the material did have a cellular or sponge - like appearance. Neville and Oswald[6] believe that the precipitate prepared by the action of an alkali on a basic cupric salt is crystalline.

A sample of the blue precipitate prepared as outlined above was air - dried for four months without undergoing any change in color. Another sample was dried over $CaCl_2$ in a desiccator for four months. At the end of this period the top layer of the precipitate had turned bluish green, while the bulk of the precipitate retained its original blue color. A sample of the blue precipitate was allowed to remain in contact with the supernatant liquid in the ice box for four months. The

top layer turned a bluish green, but the bulk of the precipitate was still blue in color. Another batch of the blue precipitate was air-dried for four days without undergoing any change in color. The material was then dried in an oven at 110°C. At the end of five hours, the blue precipitate turned green and after remaining in the oven at 110°C. over night, turned black. Samples of the blue precipitate remained under pure water for months at room temperature without any noticeable change in color. Another sample of the blue precipitate was dried over concentrated sulphuric acid in a desiccator under 5mm. pressure for four months. At the end of this period the blue precipitate had turned green but had not blackened.

Thus the cupric hydroxide prepared by the hydrolysis of the blue - violet copper ammonium sulphate at 0°C. is quite stable and differs markedly from the gelatinous precipitate prepared by the action of

alkali on a cupric salt. The latter turns black in less than a week upon exposure to air at room temperatures. No change in color was observed after keeping the blue granular precipitate for three days in contact with water at 35°C. The blue color changed to black on heating in water to 55°C, the first evidence of change being observed after about five hours and apparently complete in eight hours.

2. COMPOSITION OF THE AIR DRIED CUPRIC HYDROXIDE

Samples of the blue precipitate which had been air - dried for three days, then dried over $CaCl_2$ in a desiccator for 10 hours were carefully weighed in a tared porcelain crucible. These were heated for a period of about one hour at the full heat of a Bunsen burner, thereby changing the precipitate presumably to black CuO. The black precipitate was then weighed and the proportion of CuO to H_2O calculated. In all cases heating was repeated until two successive weighings did not differ by more than $1x10^{-4}$gms. It was found necessary to make the weighings as soon as possible after removing the crucible from the desiccator where it had cooled, due to the rather hygroscopic nature of the finely divided oxide. The heating was carried on with the oxide exposed to the air to prevent possible reduction to

Cu_2O or Cu. The results of several such determinations are shown in Table 1.

TABLE 1

Composition of the Air - Dried Cupric Hydroxide

	1	11	111
Weight of ppte.	0.2173g.	0.3477g.	0.4517g.
Weight of CuO.	0.1683g.	0.2698g.	0.3511g.
Weight of H_2O lost	0.0490g.	0.0779g.	0.1006g.
Percent loss in wt.	22.55%	22.41%	22.36%
Moles CuO in original ppte.	0.0022	0.0033	0.0044
Moles H_2O in original ppte.	0.0027	0.0043	0.0056
Formula of ppte. corresponds to	$CuO.1.29H_2O$	$CuO.1.31H_2O$	$CuO.1.27H_2O$
Average:		$CuO.1.29H_2O$	

The total loss in weight after heating over a Bunsen burner is 22.44 percent. The percentage of water by formula in $Cu(OH)_2$ or $CuO.H_2O$ is 18.55 percent. The loss in weight by our experiment is thus 3.89 percent greater than the theoretical water content, assuming that the blue precipitate corresponds to the monohydrate $CuO.H_2O$ or $Cu(OH)_2$. This may be accounted for by assuming that

some of the cupric oxide reduced to cuprous oxide, or to copper. However Mellor[22] states that the oxide is partially decomposed when the vapour pressure of the oxide attains one - fifth of that of the atmosphere; this occurs at about 1064°. The reaction is $4\ CuO \rightarrow 2\ Cu_2O + O_2$, and the porous mass reoxidizes when cooled in air. Thus even if the temperature required for the above reaction is reached, which is doubtful using a Bunsen burner, the cuprous oxide would be re-oxidized in air to cupric oxide. As for the suggestion that cupric oxide may be reduced to copper and thus account for the greater loss in weight than the theoretical, Mellor points out that for the reaction $2CuO \longrightarrow 2Cu + O_2$ to occur requires a temperature of 2500° in the electric arc. Thus the only reasonable assumption is that the blue precipitate is not the monohydrate $CuO.H_2O$ or $Cu(OH)_2$, but rather cupric hydroxide with x molecules of adsorbed water or water of hydration. It may be pointed out that the original blue precipitate may not have been

completely dried but McDonald[23] dried the precipitate in air for 5 days and calculations show that the loss in weight by his experiment is 3.28 percent greater than the theoretical water content. A sample which had been air dried for 14 days showed a value of 3.65 percent and a sample which had been dried at room temperature in a desiccator for four days showed a value of 2.69 percent greater than the theoretical water content.

Thus it appears that it is impossible to determine the composition of the blue precipitate by heating to drive off water and calculating the formula by differences.

3. PREPARATION OF DEHYDRATED CUPRIC HYDROXIDE

The blue cupric hydroxide obtained in 1.(c) was placed in a weighing bottle, and stoppered with a piece of absorbent cotton, to prevent the precipitate being blown out of the bottle when suction was later applied. The weighing bottle was suspended in a thick - walled erlenmeyer flask containing phosphorous pentoxide as a drying agent. The flask was fitted with a rubber stopper through which passed a glass tube sealed to a ground glass stopper, this served as an outlet to the vacuum pump. By this means the pressure was reduced to about 5mm. The flask and its contents were then placed in a water bath and the temperature was maintained at the boiling point for 48 hours. A constant levelling device was attached to the water bath to keep the water at the same level throughout the period of dehydration. The apparatus is shown in Figure 1.

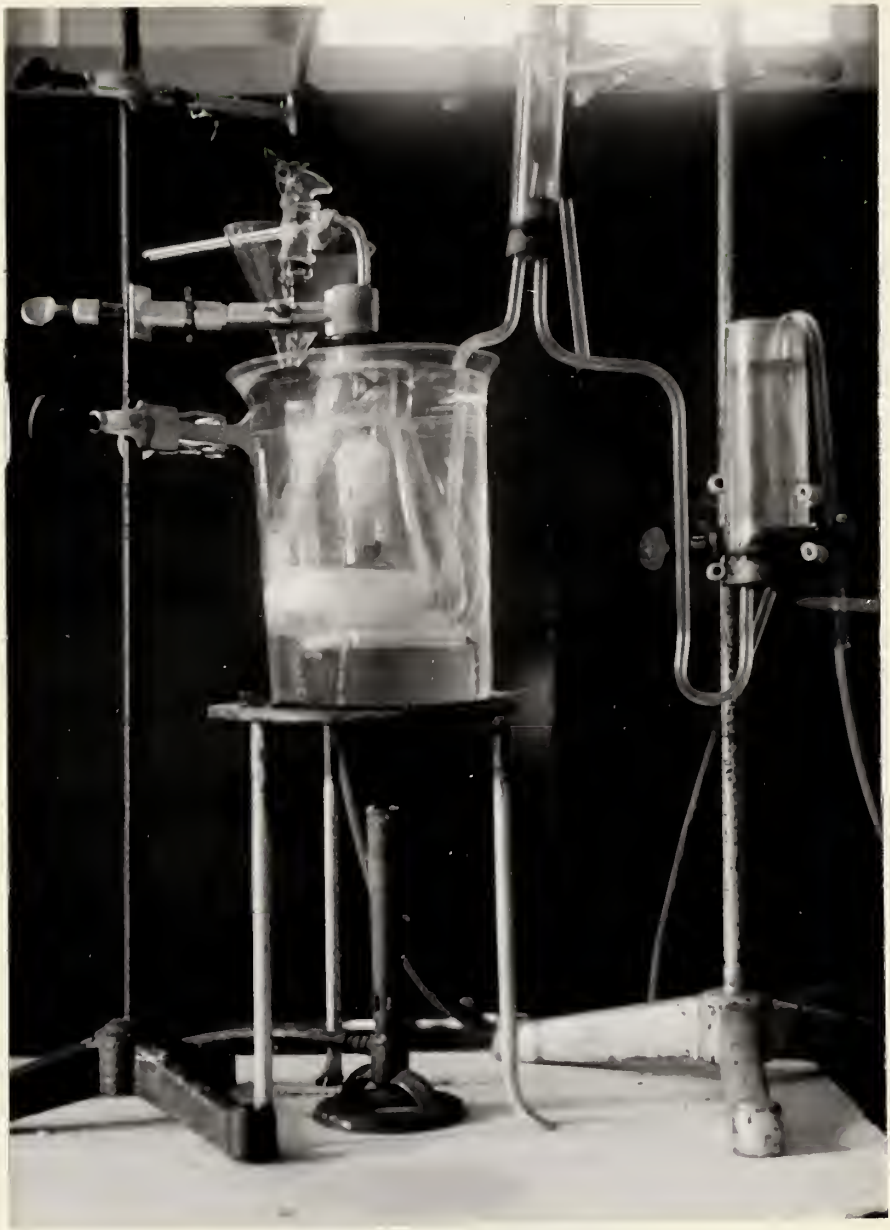

FIGURE 1

Apparatus for Dehydrating $Cu(OH)_2$.

At the end of 48 hours the blue precipitate had turned completely black. The weighing bottle was then removed, fitted with its ground glass stopper and kept in the desiccator over phosphorous pentoxide until required.

4. PREPARATION OF SINTERED CUPRIC HYDROXIDE

Some of the blue cupric hydroxide obtained in 1.(c) was placed in a clean porcelain curcible and heated at the full blast of the Meker burner for thirty minutes. The blue precipitate was changed into a black clinker like mass.

5. METHOD OF ANALYSIS

The method chosen for the analysis of the solutions for copper was

colorimetric. It was originally devised by Callan and Henderson[24] and modified by McFarlane[25] for determining concentrations of copper in biological fluids. When an aqueous solution of sodium diethyldithiocarbamate is added to a solution containing copper, the normal copper salt of diethyldithiocarbamic acid which has a golden yellow color is formed. It is claimed that this method will detect 1 part of copper in 100 million parts of distilled water. An important advantage of this method is the fact that it will give the same color with copper irrespective of the pH of the solution. The normal copper salt of diethyldithiocarbamic acid has a rather limited solubility in aqueous solution. If the amount of copper in the solution to be tested exceeds 0.015mgms. in 10c.c. the colored copper salt tends to precipitate slowly and colorimetry becomes impossible. The yellow colored substance is concentrated

in amyl alcohol and the intensity of the coloration is compared with that of a standard solution of copper. Thatcher[26] suggests the use of isoamyl alcohol, the separation occurs much more rapidly, presumably because of the greater insolubility of isoamyl alcohol in water. The color is stable for at least one hour. Cloudiness eventually develops due to the oxidation of the reagent.

Of the factors limiting the determination of the solubility of cupric hydroxide and cupric oxide in water, the method of analysing the concentrations of the solute in equilibrium with the solvent, is the most important. Therefore great care was taken in checking the colorimetric method for possible sources of error, especially since the accuracy in the range of concentrations under consideration was unknown.

For the colorimetric method to be accurate the color produced by the action of the carbonate reagent on the copper solutions must be the only color present in the solution. The original copper solution is colorless and contains no interfering metals such as iron, aluminum, chromium, zinc and others which will give a precipitate or color with the carbamate reagent.

The procedure used was as follows. In all cases water freshly redistilled from glass was used, because of copper contamination of the distilled water, in the laboratory. All glassware used was washed in nitric acid, rinsed with water and dried in an oven. Pipettes were calibrated before being used.

Copper sulphate penta-hydrate (analytical Reagent as supplied by Mallinckrodt) was first purified by recrystallizing from water. 0.3928gms.

were then weighed out and dissolved in water to which a few drops of sulphuric acid had been added, and the solution diluted to one litre so that 1c.c. corresponded to 0.10mgms. of copper. The standard solution used for comparison was prepared from the stock solution by dilution so that 1c.c. was equivalent to 10.03×10^{-4} mgms. of copper. In making the actual comparison 10c.c. of the standard solution were pipetted into a test tube, fitted with a ground glass stopper and a drop of 40 percent sodium hydroxide (Analytical Reagent, copper free) added. Then 0.5c.c. of 1 percent solution of sodium diethyldithiocarbamate (Eastman) were added. The copper salt of the diethyldithiocarbamic acid, which is a golden yellow color appeared at once. Exactly 5c.c. of freshly redistilled isoamyl alcohol (132°C. corrected) were then introduced and shaken up with the aqueous solution for one minute.

The shaking must not be too vigorous as an emulsion tends to form. The golden yellow coloration is almost completely concentrated in the alcohol layer, which separates readily on standing a few minutes. The isoamyl alcohol layer was removed by means of a pipette and filtered into one of the micro - cups of a Duboscq colorimeter. This filtration which removes the small amount of water suspended in the isoamyl alcohol layer was adapted as a time - saving measure. The isoamyl alcohol layer will become perfectly clear if allowed to stand for about 30 minutes. Using 10c.c. of the solution being tested the same procedure is followed and the intensity of color compared with that of the standard in the colorimeter.

POSSIBLE SOURCES OF ERRORS IN THE METHOD

1. From Varied Illumination

If two colors being compared

are not alike in quality, the results with varied illumination differ greatly. Daylight varies largely in intensity; passing clouds may change the reflection of direct rays. Using the standard solution (10.03×10^{-4} mgms. copper per c.c.) in both cups of the colorimeter with daylight, the average deviation was found to be 4.98 percent, with diffused light the average deviation was 0.59 percent.

The source of diffused light was a 110 watt lamp fitted into a small wooden box painted black inside. To ensure an even diffusion of light the opening of the box was covered with a piece of flashed opal glass. Thus the problem of standard lighting was answered by a source of standard artificial light. Night work with the colorimeter then became possible.

2. Mechanical Errors of the Colorimeter

Errors due to inaccurate calibration were checked by comparison of two known solutions using the standard light. The results are

shown in Table 2.

TABLE 2

Actual Concentration	Concentration Found	% Deviation
20.06×10^{-4} mgms. Cu/cc.	19.74×10^{-4} mgms. Cu/cc.	1.59
10.03×10^{-4} mgms. Cu/cc	9.93×10^{-4} mgms. Cu/cc.	1.00
10.03×10^{-4} mgms. Cu/cc	10.02×10^{-4} mgms. Cu/cc.	0.10

From the results shown we may conclude that the mechanical error of the colorimeter is negligible, since the eye cannot perceive differences of much less than 1 percent in the range of greatest accuracy.

3. Accuracy of the Method

The accuracy of the method was determined by comparing solutions of known copper concentrations with the standard solution of a concentration approximately that expected in the solubility determinations. A series of solutions containing known concentrations of copper from

4.03×10^{-4} mgms. to 2.5×10^{-3} mgms. per c.c. was made up and compared with the standard solution (10.03×10^{-4} mgms. copper per c.c.). The results are shown in Table 3, and Figure 2.

TABLE 3.

Color Read.	Theor. Read.	Actual Conc. mgms. Cu/cc.	Exp. Found Conc. mgms. Cu/cc.
38.05	37.39	25.0×10^{-4}	25.47×10^{-4}
25.31	30.00	20.06×10^{-4}	16.93×10^{-4}
21.79	22.46	15.02×10^{-4}	14.57×10^{-4}
14.86	15.00	10.03×10^{-4}	9.93×10^{-4}
7.45	6.02	4.03×10^{-4}	4.98×10^{-4}

Colorimeter readings are the average of 10 readings, 5 approaching the color from the lighter side and 5 from the more intense side.

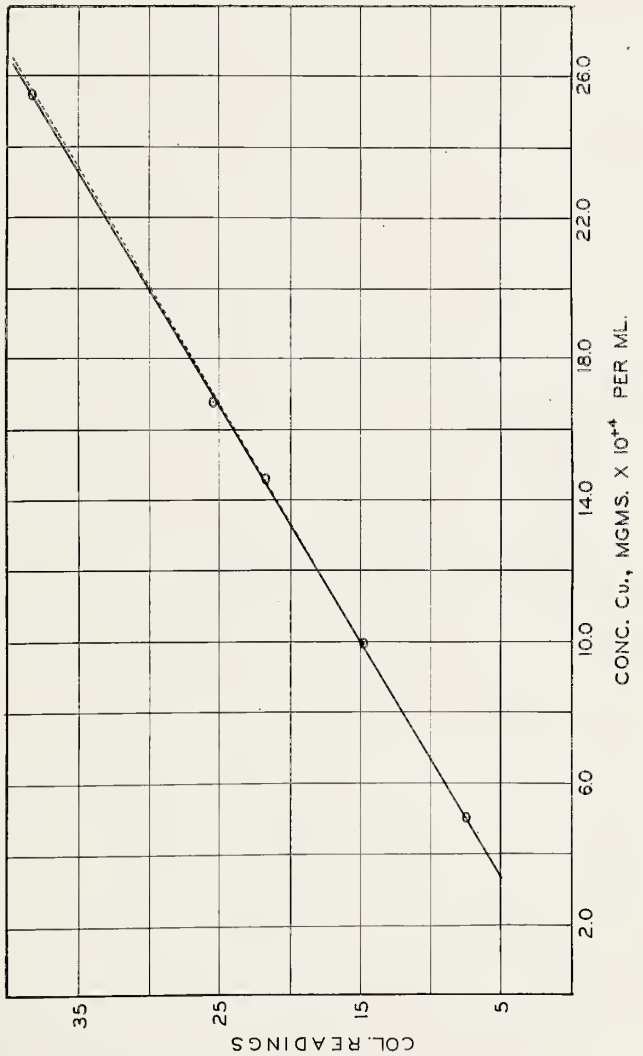

FIGURE 2.

Accuracy of the Method

In figure 2, the full line represents the experimentally found concentrations, the dotted line represents the actual concentrations. It will be seen that the maximum error in the range investigated occurs when the difference in concentration between the standard and the solution tested is a maximum. That is, best results will be obtained when the standard and the solution to be tested are of mearly the same concentration. From figure 2, it is evident that the range of maximum sensitivity is between 2.00×10^{-4} mgms. and 14.00×10^{-4} mgms. copper per c.c. using 10.03×10^{-4} mgms. copper per c.c. as the standard. The solubilities actually found averaged 3.00×10^{-4} mgms. copper per c.c. and as such fell in the range of maximum sensitivity.

6. PREPARATION OF SATURATED SOLUTIONS

The cupric hydroxide freshly prepared from 1(c), by the hydrolysis of the blue - violet copper ammonium sulphate at 0°C. was kept in water not more than two days before being used. The carefully washed solid was mechanically stirred

for two hours in water freshly redistilled from Pyrex and kept at a temperature of ± 0.20°C. of that desired. After settling for half an hour samples were withdrawn for analysis by means of gentle suction through a 'stick filter' three thicknesses of Whatmans No.2, filter paper being the filtering medium. The first 20 or 30 c.c. of the filtrate were discarded. A drop of dilute sulphuric acid was added to the receiver before collecting the sample in order to keep the copper in solution.

Using the blue cupric hydroxide freshly prepared and the method of obtaining a saturated solution as outlined above, no aggreement could be obtained between successive determinations with the same sample at a definite temperature. The variation in the results between determinations at the same temperature was more than could be attributed to experimental error or to the limitations of the analytical procedure. It was noticed that when the diethyldithiocarbamate reagent and the isoamyl alcohol were added to the copper solutions a turbidity or cloudiness developed. This suggested

the presence of colloids. A sample which had come to equilibrium was removed using the stick-filter exactly as above and tested for the presence of colloids. A strong beam of light was concentrated on the solution and the path of the light in the solution was illuminated by a bluish opalescence. This phenomenon known as the Tyndall effect is caused by particles, smaller than the wave lenght of the light which scatter the light, thereby polarizing it at the same time. To make sure that the bluish opalescence was not due to fluorescence of the substance itself, a Nicol prism was interposed between the source of light and the solution. Upon rotating the prism, the bluish opalescence or light cone appeared to be partly or completely extinguished in certain positions, showing that the light was polarized. Water redistilled from glass was then tested and a faint Tyndall cone was noticed. However the copper hydroxide solution gave a Tyndall effect which was many times more pronounced than that with water. A number of known colloidal solutions, such as arsenic trisulfide ferric hydroxide and

aluminium hydroxide were tested and each showed a prominent Tyndall cone. Copper sulphate solution gave no Tyndall effect. Copper nitrate solution showed a faint bluish opalescence, however upon observing the light cone through a mounted Nicol prism, the light cone did not disappear when the prism was rotated. Thus the bluish cone was probably due to fluorescence of the copper nitrate itself.

The anomalous results obtained were apparently due to colloidal copper hydroxide. In the case of true solubilities we are dealing with true equilibrium, i,e., equilibria attainable from either side and the solubility is independent of the amount of solute present. True solubilities depend only on the temperature, and, to a lesser degree, on the pressure, always assuming that the solute does not consist of very small particles. Even here, then, the degree of dispersion appears as a variable. Below a certain particle size the solubility of substances shows a rapid increase with decreasing particle size, but becomes practically independent of particle

size in the case of larger particles. The validity of the laws of solubility is a necessary condition for the applicability of the law of mass action to the solubility phenomena of dilute electrolytes, as formulated in the theory of the solubility product. However generally applicable the laws of solubility may be for true solutions, they lose their validity for any processes of solution or of dispersion, which lead to the formation of colloidal systems. In many cases of colloidal solutions equilibrium is generally not attainable from both sides, and is not dependent on temperature alone. The structure and particle size of the solute, its previous history, and its age has a marked influence on its final condition. Colloidal solubility is not independent of the quantity of solute present. The concentration of colloidally dissolved substances either increases continuously with the quantity of solute present, or it shows a maximum for an intermediate quantity of solute. Thus the active mass of a colloidally dispersed substance, or a substance in the process of being colloidally dispersed is

not independent of its quantity.

Therefore in order to proceed with the problem it became necessary to remove the colloidal copper hydroxide. Dialysis was suggested. In this way it was thought that true (molecularly disperse) copper hydroxide solution would dialyze out, leaving the colloidal copper hydroxide in the dialyzer. The blue copper hydroxide was therefore placed in an animal parchment bag and suspended in water. The solution was stirred at 25°C. and samples were removed every 3 hours. After remaining in contact with the solution for 24 hours, the animal parchment began to impart a yellow coloration to the solution. Since a colorimetric method was being used for analysis, dialysis with animal parchment had to be abandoned. Dialysis using a collodion membrane required too long to come to equilibrium, but stirring inside the dialyzer as well as outside shortened the time necessary for equilibrium to be reached.

The collodion membrane was prepared from a 24 percent alcohol collodion solution

(Eimer and Amend). The membrane was fitted to a one - holed rubber stopper and securely fastened by means of some of the collodion solution. The stopper was then wired to a wooden cover which fitted a litre beaker. By this means it was possible to effect stirring inside and outside the dialyzer. Figure 3 shows the dialyzer and method of stirring.

FIGURE 3.

DIALIZER.

In order to ascertain the exact period of time necessary for equilibrium to be established using the collodion membrane, a series of preliminary runs were carried out. The results are shown in Table 4.

TABLE 4.

Run	Temp.	Time	Concentration Found
1 (a)	25°C.	4 hours	1.73×10^{-4} mgms. Cu/cc.
(b)	25°C.	6 hours	2.05×10^{-4} mgms. Cu/cc.
(c)	25°C.	10 hours	2.30×10^{-4} mgms. Cu/cc.
(d)	25°C.	22 hours	2.25×10^{-4} mgms. Cu/cc.
(e)	25°C.	23 hours	2.34×10^{-4} mgms. Cu/cc.
2 (a)	35°C.	10 hours	3.70×10^{-4} mgms. Cu/cc.
(b)	35°C.	14 hours	3.66×10^{-4} mgms. Cu/cc.
3 (a)	45°C.	5 hours	2.42×10^{-4} mgms. Cu/cc.
(b)	45°C.	12 hours	2.41×10^{-4} mgms. Cu/cc.
4 (a)	55°C.	51/2 hours	2.68×10^{-4} mgms. Cu/cc.
(b)	55°C.	101/2 hours	2.56×10^{-4} mgms. Cu/cc.

The preliminary determinations showed that 10 hours stirring was sufficient for equilibrium to be established in the temperature range 25°C. to 35°C. and 5 hours from 45°C. up. For equilibrium to be reached at temperatures below 25°C, 20 hours stirring was allowed. Equilibrium could not be established above a temperature of 85°C, because the solution evaporated too quickly.

RESULTS

The solubility results for the cupric hydroxide freshly prepared by method 1(c) from the blue - violet copper ammonium sulphate at 0°C, are given in Tables 5,6,and Figure 4.

TABLE 5

Solubility of Copper Hydroxide

Temp (±0.20°C)	Mgms. Cu per c.c. 1	2	3	Average Mgms. Cu/c.c.
0°	1.14×10^{-4}	1.17×10^{-4}		1.16×10^{-4}
10°	1.35x "	1.40x "	1.39×10^{-4}	1.38x "
20°	2.02x "	2.01x "	2.05x "	2.03x "
25°	2.25x "	2.34x "	2.30x "	2.30x "
30°	2.76x "	2.68x "	2.62x "	2.69x "
35°(a)	3.65x "	3.75x "	3.67x "	3.69x "
35°(b)	3.60x "	3.57x "		3.60x "
35°(c)	3.75x "	3.73x "		3.74x "
45°	2.41x "	2.43x "	2.42x "	2.42x "
55°	2.69x "	2.57x "		2.65x "
65°	2.74x "	2.72x "		2.73x "
75°	2.98x "	3.11x "		3.05x "
85°	3.61x "	3.54x "	3.60x "	3.58x "

The blue precipitate turned green in the neighborhood of 45°C, and at a temperature of 55°C, the precipitate appeared completely black. The values at 30°C. were obtained using a different sample and a freshly prepared dialyzer. The values at 35°C(b) and 35°C(c) were obtained using another freshly prepared sample, in each case, and a new dialyzer. The values found at 30°C. and 35°C(b) and 35°C(c) indicate that the solubility values of copper hydroxide are reproduceable.

Table 6 shows the solubility of the cupric hydroxide in mgms. copper per c.c, mgms. $Cu(OH)_2$ per litre, and moles $Cu(OH)_2$ per litre.

TABLE 6

Solubility of Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu/cc.	Mgms. $Cu(OH)_2$ per litre	Moles $Cu(OH)_2$ per litre
0°	1.16×10^{-4}	17.8×10^{-2}	1.8×10^{-6}
10°	1.38x "	21.2x "	2.2x "
20°	2.03x "	31.2x "	3.2x "
25°	2.30x "	35.2x "	3.6x "
30°	2.69x "	41.3x "	4.2x "
35°	3.68x "	56.6x "	5.8x "
45°	2.42x "	37.1x "	3.8x "
55°	2.65x "	40.2x "	4.2x "
65°	2.73x "	41.9x "	4.3x "
75°	3.05x "	46.8x "	4.8x "
85°	3.58x "	55.0x "	5.6x "

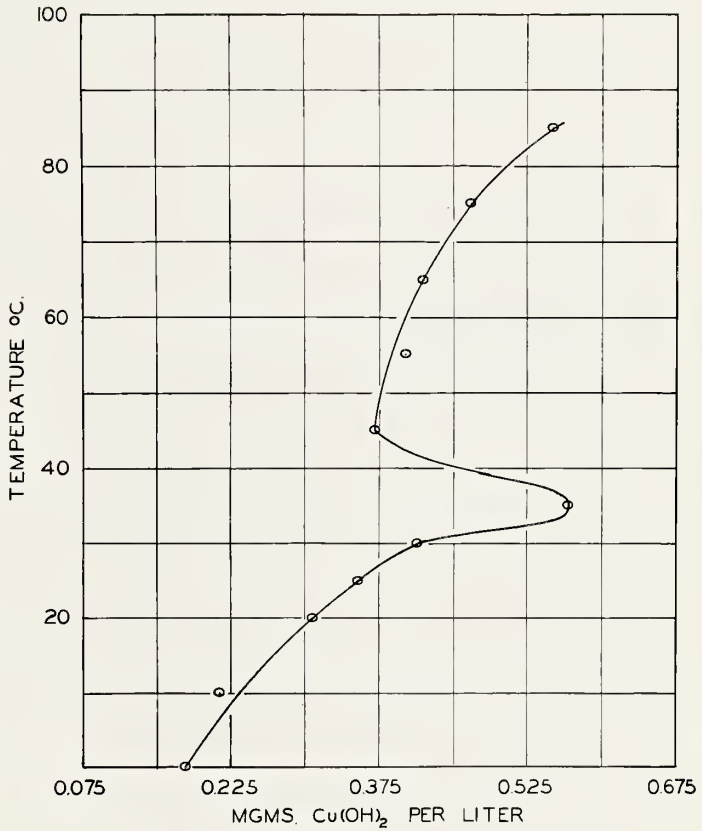

FIGURE 4.

SOLUBILITY OF COPPER HYDROXIDE

Tables 7,8 contain the results for the solubility of the partially dehydrated copper hydroxide obtained by heating the blue cupric hydroxide in water to 85°C. These are shown graphically in Figure 5.

TABLE 7

Solubility of Partially Dehydrated Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu per c.c. 1	2	3	Average Mgms. Cu/c.c.
0°	2.68×10^{-4}	2.60×10^{-4}	2.59×10^{-4}	2.62×10^{-4}
10°	2.96x "	3.02x "		2.99x "
20°	3.57x "	3.17x "	3.15x "	3.29x "
35°	4.79x "	4.83x "	4.93x "	4.85x "
40°	3.66x "	3.59x "	3.80x "	3.68x "
45°	2.74x "	2.69x "	2.74x "	2.72x "
55°	2.69x "	2.54x "	2.79x "	2.67x "
65°	2.74x "	2.72x "		2.73x "
75°	2.98x "	3.11x "		3.05x "
85°	3.61x "	3.54x "	3.60x "	3.58x "

The solubility of the partially dehydrated copper hydroxide in mgms. Cu per c.c., Mgms. CuO per litre, and Moles CuO per litre are shown in Table 8.

TABLE 8

Solubility of Partially Dehydrated Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu per c.c.	Mgms. CuO. per litre	Moles CuO per litre
0°	2.62×10^{-4}	32.8×10^{-2}	4.1×10^{-6}
10°	2.99x "	37.4x "	4.7x "
20°	3.29x "	41.2x "	5.2x "
35°	4.85x "	60.7x "	7.6x "
40°	3.68x "	46.0x "	5.8x "
45°	2.72x "	34.0x "	4.3x "
55°	2.67x "	33.0x "	4.1x "
65°	2.73x "	34.2x "	4.3x "
75°	3.05x "	38.2x "	4.8x "
85°	3.58x "	44.8x "	5.6x "

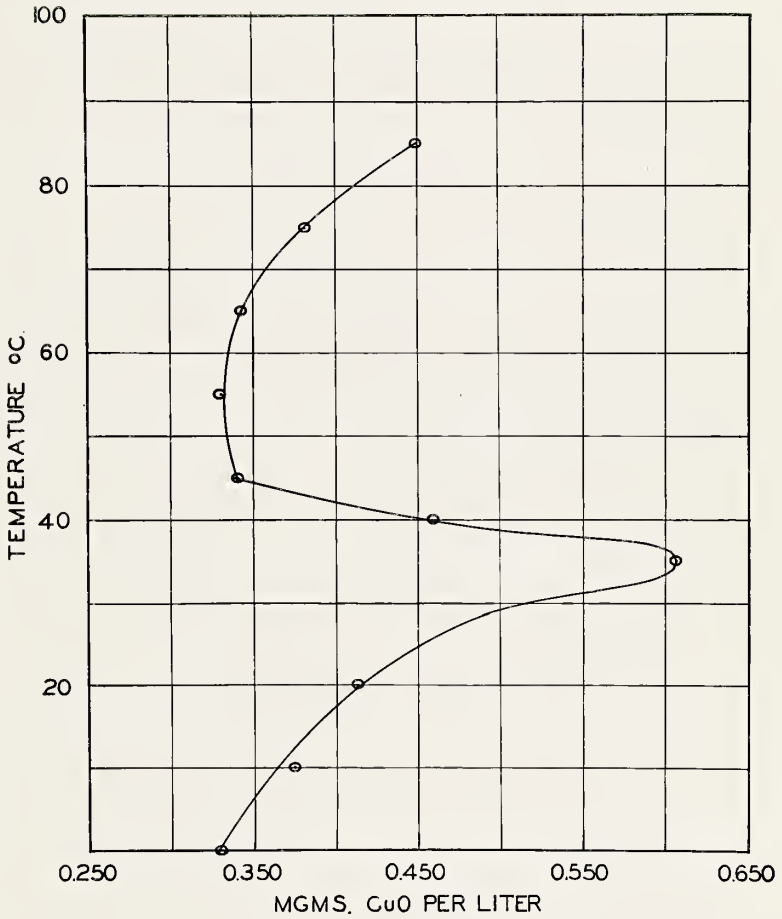

FIGURE 5.

SOLUBILITY OF PARTIALLY DEHYDRATED COPPER HYDROXIDE

The solubility results of the copper hydroxide dehydrated over phosphorous pentoxide under 5 mm. pressure and at 97°C. are shown in Tables 9 and Figure 6.

TABLE 9

Solubility of Dehydrated Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu per c.c. 1	2	3	Average Mgms. Cu/c.c.
0°	1.28×10^{-4}	1.01×10^{-4}	1.09×10^{-4}	1.17×10^{-4}
		1.20x "	1.28x "	
15°	1.11x "	1.30x "	1.25x "	1.23x "
			1.24x "	
25°	1.56x "	1.56x "	1.58x "	1.57x "
35°	1.75x "	1.60x "	1.81x "	1.72x "
45°	2.01x "	1.99x "	2.04x "	2.02x "
55°	2.05x "	2.23x "	2.08x "	2.12x "
65°	2.46x "	2.47x "	2.42x "	2.43x "
			2.38x "	
75°	2.69x "	2.70x "	2.69x "	2.69x "
85°	3.01x "	3.00x "	2.94x "	2.98x "

The solubility of the dehydrated copper hydroxide in Mgms. Cu per c.c., Mgms CuO per litre and Moles CuO per litre are shown in Table 10.

TABLE 10

Solubility of Dehydrated Copper Hydroxide

Temp. (±0.20° C)	Mgms. Cu per c.c.	Mgms. CuO. per litre	Moles CuO per litre
0°	1.17×10^{-4}	14.6×10^{-2}	1.8×10^{-6}
15°	1.23x "	15.4x "	1.9x "
25°	1.57x "	19.7x "	2.5x "
35°	1.72x "	21.5x "	2.7x "
45°	2.02x "	25.3x "	3.2x "
55°	2.12x "	26.5x "	3.3x "
65°	2.43x "	30.4x "	3.8x "
75°	2.69x "	33.7x "	4.2x "
85°	2.98x "	37.3x "	4.7x "

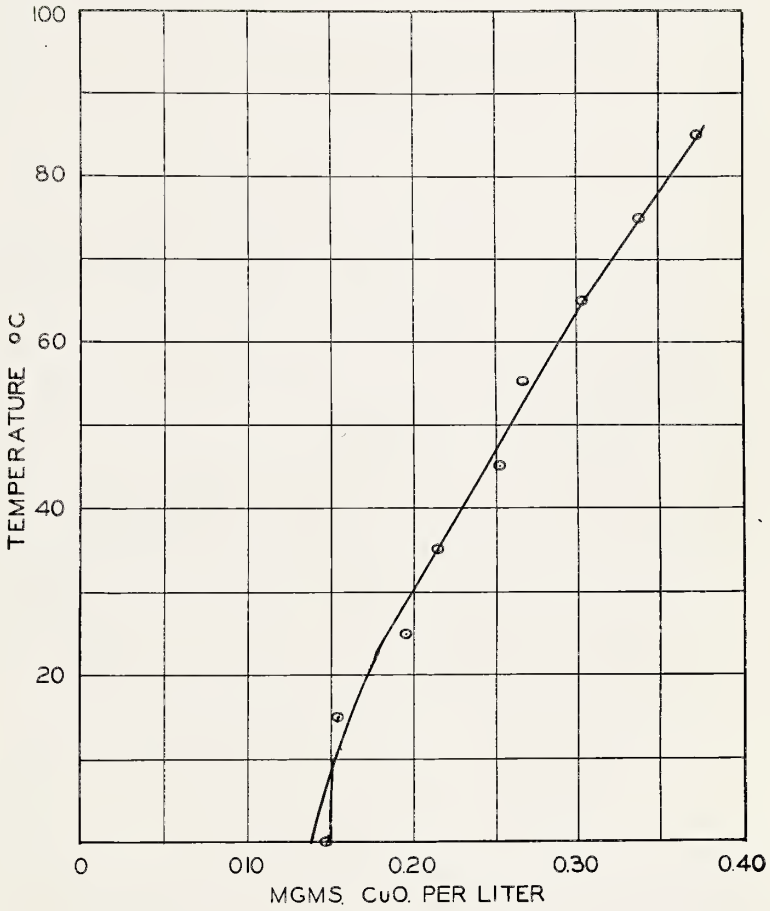

FIGURE 6.

SOLUBILITY OF DEHYDRATED COPPER HYDROXIDE

Table 11 shows the solubility results of sintered copper hydroxide prepared by heating the blue copper hydroxide with the full blast of the Meker burner for half an hour.

TABLE 11

Solubility of Sintered Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu per c.c. 1	2	3	Average Mgms. Cu/c.c.
35°	1.60×10^{-4}	1.89×10^{-4}	1.72×10^{-4}	1.73×10^{-4}
55°	2.09x "	2.11x "	2.10x "	2.10x "
65°	2.38x "	2.50x "	2.49x "	2.44x "

The solubilities of the sintered copper hydroxide in Mgms. Cu per c.c., Mgms CuO per litre and Moles CuO per litre are shown in Table 12.

TABLE 12

Solubility of Sintered Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu per c.c.	Mgms. CuO. per litre	Moles CuO per litre
35°	1.73×10^{-4}	21.6×10^{-2}	2.7×10^{-6}
55°	2.10x "	26.3x "	3.3x "
65°	2.44x "	30.5x "	3.8x "

The values of the solubilities of the sintered copper hydroxide coincided with those of the copper hydroxide dehydrated over phosphorous pentoxide under 5 mm. pressure at 97°C. Thus we can conclude that the values in Tables 9 and 11 are the solubility values of anhydrous CuO.

Table 13 contains the results obtained for the solubility of the blue copper hydroxide prepared from method 1(c), by hydrolyzing the blue - violet copper ammonium complex at 0°C, and allowed to remain in water at room temperature for one month.

TABLE 13

Solubility of Aged Copper Hydroxide

Temp. (±0.20°C)	Mgms. Cu per c.c. 1	2	3	Average Mgms. Cu/c.c.
25°	1.79×10^{-4}	1.83×10^{-4}	1.76×10^{-4}	1.79×10^{-4}
35°	2.06x "	2.11x "	2.04x "	2.07x "
45°	2.51x "	2.42x "	2.44x "	2.45x "
85°	3.51x "	3.54x "	3.56x "	3.54x "
25°(a)	2.75x "	2.74x "	2.58x "	2.69x "

The solubility value shown at 25°(a) was obtained by starting with the aged copper hydroxide

at a temperature of 85°C, and cooling the solution down to 25°C. with constant stirring until equilibrium was reached.

The solubilities of the aged copper hydroxide in Mgms Cu per c.c., Mgms $Cu(OH)_2$ per litre, and Moles $Cu(OH)_2$ per litre are shown in Table 14.

TABLE 14

Solubility of Aged Copper Hydroxide

Temp. ($\pm$0.20°C)	Mgms. Cu/cc.	Mgms. $Cu(OH)_2$ per litre	Moles $Cu(OH)_2$ per litre
25°	1.79×10^{-4}	27.5×10^{-2}	2.8×10^{-6}
35°	2.07x "	31.8x "	3.3x "
45°	2.45x "	37.6x "	3.9x "
85°	3.54x "	54.4x "	5.6x "
25°(a)	2.69x "	41.3x "	4.2x "

The solubility values obtained with the aged cupric hydroxide differ markedly from the values obtained with the freshly prepared cupric hydroxide. This seems to indicate that we are dealing with two different forms of cupric hydroxide, the variable factor probably being water of hydration.

Comparison of the solubilities of sintered copper hydroxide, dehydrated copper hydroxide, copper hydroxide, and partially dehydrated copper hydroxide is shown in Figure 7.

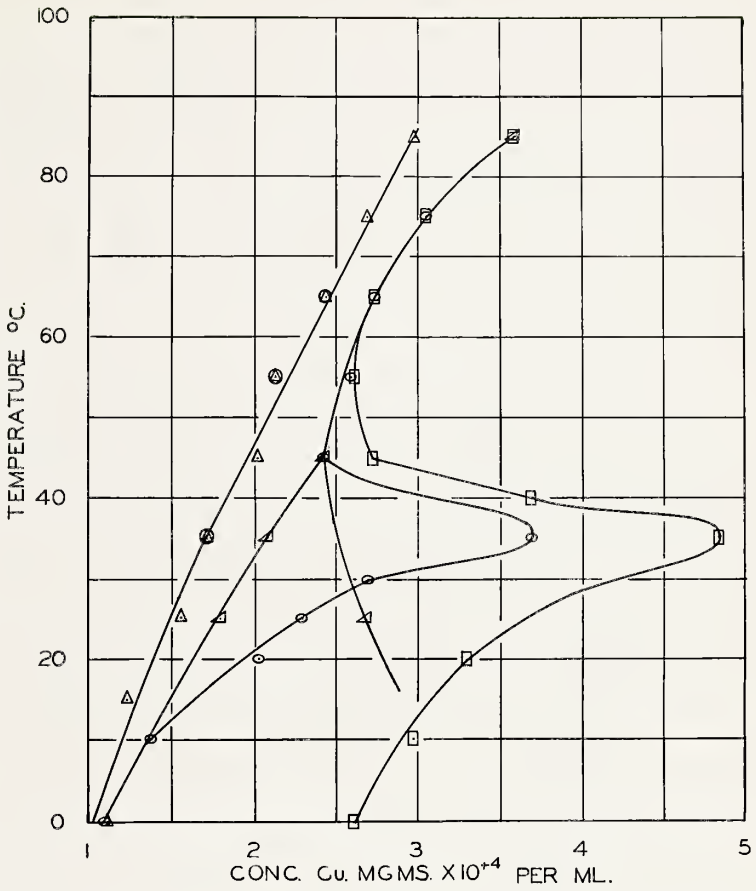

FIGURE 7.

DEHYDRATED COPPER HYDROXIDE
SINTERED COPPER HYDROXIDE
AGED COPPER HYDROXIDE
FRESH COPPER HYDROXIDE
PARTIALLY DEHYDRATED COPPER HYDROXIDE

DISCUSSION

The solubility curves obtained differ markedly in that they possess no general form. This, however, is not to be regarded as uncommon, for it is known that the solubility curve may have a variety of shapes or forms. The solubility curve may have an almost straight and horizontal course, or slope upwards at varying angles; it may even slope downwards corresponding to a decrease in solubility with a rise in temperature. It may exhibit maxima or minima of solubility, or may show discontinuities associated with phase changes, due to reaction with the solvent or polymorphism. Thus the slope of the solubility curve may vary in any fashion, as long as the variation of solubility with temperature is in accordance with the Principle of Le Chatelier, as expressed quantitatively in vant Hoff's equation.

$$\frac{d\ln S}{dT} = \frac{\Delta H}{RT^2}$$

where S is the solubility, T the absolute temperature

and ΔH the integral heat of solution. It follows therefore, that an increase of solubility with rise of temperature must occur in those cases where the process of solution is accompanied by an absorption of heat; and a decrease in solubility with rise of temperature will be found in cases where solution occurs with the evolution of heat. When there is no heat effect accompanying solution, change of temperature will have no influence on the solubility. No measurements of the heat of solution were attempted in this work. It may be pointed out that since the solubility of cupric hydroxide and cupric oxide in water is of such a low order, great difficulty would be encountered in attempting to measure directly the heats of solution of these substances. An approximation can of course be obtained using the slope of the curve.

Despite its many forms the solubility curve for any given substance is continuous, as long as the solid phase remains unchanged. If any discontinuity of the curve occurs, it is a sign

that the solid phase has undergone alteration. Since the composition of the solid phases present were not ascertained, excepting that of CuO, we can only offer hypotheses as to the probable constitution of the solid phases. Figure 8, shows the Phase diagram of cupric hydroxide and water.

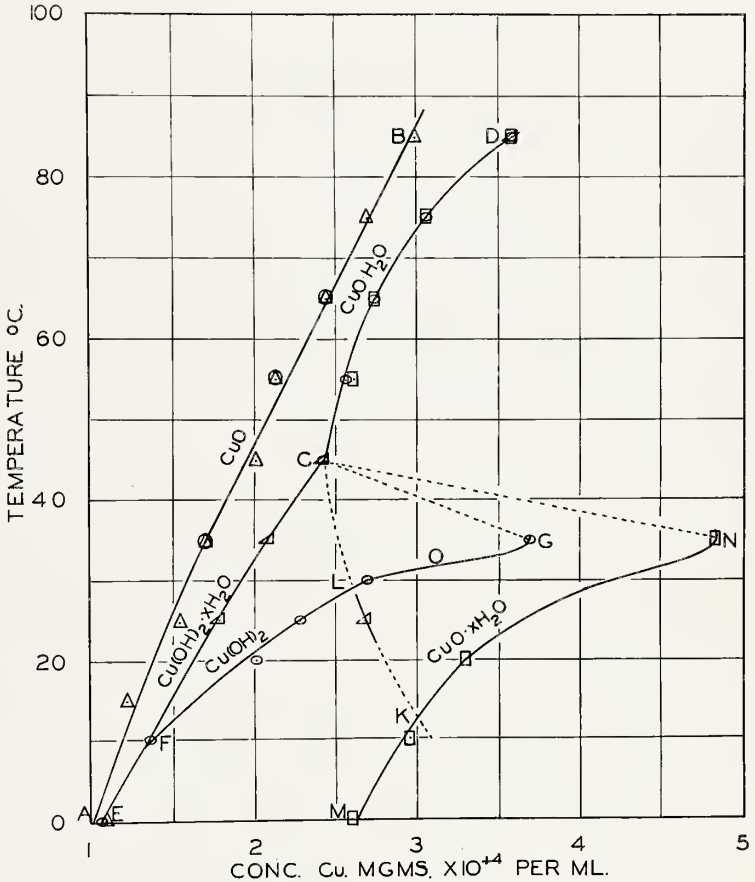

FIGURE 8.

PHASE DIAGRAM

At 0°C. cupric hydroxide was precipitated out of solution forming the blue precipitate which is microscopically crystalline $Cu(OH)_2$ as shown by Neville and Oswald[6]. The solubility in water of this fresh blue precipitate increased as the temperature was raised; the value of the solubility is represented graphically by curve FG, and given in Table 6. At temperatures above that corresponding to G, it was found that the solubility no longer increased but decreased with rise in temperature. At the same time it was noted that the solid phase above 45°C. gradually turned black while that in contact with the solution at temperatures below 45°C. remained blue. The blue solid phase in equilibrium with the solution below 45°C. was $Cu(OH)_2$, while the black solid phase at temperatures above 45°C. may be $CuO.H_2O$. The course of the solubility curve of $CuO.H_2O$ is shown by the curve CD, and the values of the solubility are given in Table 6 and 7.

The curve AB, has been shown by experiment to represent the solubility of anhydrous CuO.

The solubility values obtained with the sintered CuO agreed with those obtained with the CuO formed by dehydrating the blue $Cu(OH)_2$ over phosphorous pentoxide under 5mm. pressure, and at a temperature of 97°. The solubility curve CD, evidently represents the behaviour of the stable form to which the $Cu(OH)_2$ reverts upon being heated to a temperature above 45°C. It would be expected that the solubility curve CD, should coincide with the solubility curve of anhydrous CuO, AB, but since this is not the case, it is assumed that the curve CD, represents the solubility of a hydrated CuO. i.e., $CuO.H_2O$. The blue cupric hydroxide prepared at 0°C, by method 1(c), after aging in pure water gave a different solubility curve from that of the freshly prepared cupric hydroxide. The solubility of the aged blue cupric hydroxide increased as the temperature was raised. This is represented graphically by curve EC. The difference in solubility between the aged and the fresh cupric hydroxide is clearly shown by the variation in the slopes of the two curves EC and FG. This difference in solubility

between the aged and the freshly prepared cupric hydroxide can be attributed to a difference in hydration. Hence, if the fresh cupric hydroxide is $Cu(OH)_2$, then the aged precipitate may be represented by the formula $Cu(OH)_2.xH_2O$. One might with equal reason represent the aged blue form as an allotrope of the fresh blue precipitate. However, for the purpose of this discussion, the hydrate is favoured.

Since each solid substance has its own solubility curve, there are three separate curves to be considered in the case of cupric hydroxide and water. Where two curves intersect the solution must be saturated with respect to two solid phases. At the point C, therefore, the point of intersection of the solubility curves of $CuO.H_2O$ and $Cu(OH)_2.xH_2O$, the solution must be saturated with respect to these two solid substances. Applying the Phase Rule, $F = C+2-P$, we have at this point, a two component system existing in four phases, $CuO.H_2O$, $Cu(OH)_2.xH_2O$, solution, and water vapor. The system is therefore invariant. If one of the factors, pressure, temperature, or concentration of

components remains constant, then the system becomes a condensed system and as such the Phase Rule is $F = C-P+1$ and for a two component system $F = 3-P$. This is the case when solubilities are determined in open vessels, the pressure is then equal to atmospheric pressure. Under these conditions, then, the system $CuO.H_2O$, $Cu(OH)_2.xH_2O$ and solution, will possess no degree of freedom, and can exist, therefore, only at one definite temperature and when the solution has a certain definite composition. Thus C is a triple point and the temperature of this point is 45°C. At this point the solution contains 3.8×10^{-6} moles $CuO.H_2O$ per litre.

The solubility curve of $CuO.H_2O$ has been followed to a temperature below 45°C. Below this temperature, however, the solubility of $CuO.H_2O$ is greater than that of $Cu(OH)_2.xH_2O$. The saturated solution of $CuO.H_2O$ will therefore be supersaturated with respect to $Cu(OH)_2.xH_2O$ and will deposit this substance if a 'nucleus' is added to the solution. The $CuO.H_2O$ below 45°C. should and probably would change over to $Cu(OH)_2.xH_2O$ if

sufficient time were allowed for the transformation to take palce. This, however was not done. From this we see that at temperatures above 45°C. $CuO.H_2O$ is the stable form, while $Cu(OH)_2.xH_2O$ is unstable, at temperatures below 45°C. $Cu(OH)_2.xH_2O$ is stable. This temperature, therefore, is the transition temperature for $Cu(OH)_2.xH_2O$ and $CuO.H_2O$.

$Cu(OH)_2$ is stable with respect to $CuO.H_2O$ until the point L is reached. From L to G $Cu(OH)_2$ is metastable with respect to $CuO.H_2O$ and the transformation from $Cu(OH)_2$ to $CuO.H_2O$ begins to take place at a temperature (35°C) below the transition temperature (45°C), so that when the triple point C is reached $Cu(OH)_2$ had disappeared and only $CuO.H_2O$ remains.

From Figure 8, it appears that at all temperatures the solubility of $Cu(OH)_2$ is greater than that of $Cu(OH)_2.xH_2O$. Therefore the former solid phase must be metastable with respect to the latter, so that throughout its whole course, the solubility curve of the $Cu(OH)_2$ represents a metastable equilibria. This follows from the fact,

that the metastable phase always has the greater solubility and if it were present with the stable phase it would necessarily change into the less soluble stable phase. Thus it is probable, that a sample of $Cu(OH)_2$ maintained at a temperature corresponding to point O, would eventually change over to $CuO.xH_2O$, the stable form. Similarily, since at all temperatures $Cu(OH)_2.xH_2O$, $CuO.H_2O$, and $Cu(OH)_2$ are all more soluble than CuO, therefore, the former solid phases must be metastable with respect to the latter. Thus all the solubility curves except AB represent metastable equilibria. Of course, this does not mean that the forms other than CuO will revert to CuO at ordinary temperatures, in reasonable time. While the systems may be metastable, they may also be 'suspended equilibria', in other words permanent, such as mixtures of hydrogen and oxygen at ordinary teperatures.

The solubility curve MN is the only curve which is not explicable on the basis of the phase relations developed above. The curve MN was

realized by starting with black $CuO.H_2O$ at a temperature of 85°C. and making solubility measurements at temperature intervals down to 0°C. From the phase relationships shown, this means that $CuO.H_2O$, the stable form is changing over to a metastable modification $CuO.xH_2O$, along the line CN. This of course, on the basis of thermodynamics is impossible. If we had started with $CuO.xH_2O$, at the point M and traced out the curve MN with increasing temperatures, then the curve MN would be in agreement with the rest of the phase relations developed above. For then, $CuO.xH_2O$ would be stable with respect to $CuO.H_2O$ until the point K is reached. From K to N, $CuO.xH_2O$ would be metastable with respect to $CuO.H_2O$ and the transformation from $CuO.xH_2O$ to $CuO.H_2O$ would begin at a temperature below the transition temperature, and when the triple point C was reached only $CuO.H_2O$ would exist. At present the anomalous behaviour shown by the solubility curve MN can only be attributed to some external factor such as the collodion membrane. It should be pointed out, that

the curve MN was not reproduced and represents a single series of determinations. On the other hand, the curve FG was found to be reproduceable.

The dialyzer containing the black precipitate remained in contact with the solution about two weeks before the curve MN was completed and within this time the dialyzer may have undergone some change.

Disregarding the solubility curve MN, the phase diagram developed bears a general resemblance to that of Na_2SO_4 (Wuite[27]) and to that of $CaCrO_4$ (Myluis and von Wrochem[28]). In view of the phase relations developed above the discordant results reported, by other workers, for the solubility of cupric hydroxide may be explained. It is readily seen, from Figure 8, that at a temperature of, say, 25°C, three different saturated solutions of cupric hydroxide are possible, each in equilibrium with one of the following proposed solid phases. $Cu(OH)_2.xH_2O$, $Cu(OH)_2$, or $CuO.H_2O$. Two of these solutions, however, would be metastable with respect to

$Cu(OH)_2.xH_2O$. The solubility value, obtained in the absence of control and knowledge of the material used, might be anyone of three values.

As noted in the Introduction, the solubility of cupric oxide as determined conductimetrically by Remy and Kuhlman[1] is 6.7×10^{-5} moles per litre at 20°C. The value obtained by using the method above is 2.2×10^{-6} moles per litre at 20°C. However, Remy and Kuhlman's value may be in error due to the decrease in electrical conductivity caused by the adsorption of alkali by the cupric hydroxide for its pepitzation and replacement of hydroxyl ions by cuprate ions. A decrease in conductivity will result in an enhanced value for the solubility. McDowell and Johnston[5] obtained a value of 2.9×10^{-5} moles per litre for the oxide at 25°C. The value found above is 2.5×10^{-6} moles per litre at 25°C. However, McDowell and Johnston point out, that their value is only a rough approximation, because they were faced with the difficulty of the copper solution coming out colloidal.

In conclusion it is evident that the work reported opens up a field for investigation, mainly the characterisation of the solid phases postulated above.

SUMMARY.

1. The blue cupric hydroxide has been prepared by three methods.

2. The cupric hydroxide prepared by the hydrolysis of the blue - violet copper ammonium sulphate is the most stable.

3. Anhydrous cupric oxide has been prepared by dehydrating the blue cupric hydroxide in two ways.

4. Dialysis through a collodion membrane overcomes the difficulty of the saturated solution coming out colloidal.

5. The solubility of freshly prepared cupric hydroxide and aged cupric hydroxide has been determined over the temperature range 0°C. to 85°C. At temperatures below 45°C. the solubility value obtained in the absence of control, and knowledge of the material used, might be any one of three values.

6. The solubility of partially dehydrated cupric hydroxide and anhydrous cupric oxide has been determined over the temperature range 0°C. to 85°C. The solubility of anhydrous cupric oxide at 25°C. is 2.5×10^{-6} moles per litre.

7. A discussion of the results has been given and the phase relations of cupric hydroxide, cupric oxide and water have been considered.

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